106 °C (0.7 kPa) [lit.[16] bp 156 °C (2.1 kPa)]. Similarly, the following eight amides and *N,N*-diethylacetamide were obtained from the reactions of the corresponding carboxylic acids and amines. Solid amides were recrystallized from EtOAc/hexane. **N-Propyldichloroacetamide ($Cl_2CHCONHPr$)**: bp 67 °C (0.8 kPa); IR (KRS-5) 1700 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (br, 1 H, N*H*), 4.60 (s, 1 H, CCl_2H), 4.03 (t, 2 H, J = 6.0 Hz, NCH_2), 1.80 (sextet, 2 H, CH_2), 0.91 (t, 3 H, J = 6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 185.3 (s, *C*=O), 68.7 (d, CCl_2H), 47.7 (t, NCH_2), 20.7 (t, CH_2), 11.2 (q, CH_3); MS m/z 169 (M^+, ^{35}Cl). Anal. Calcd for $C_5H_9Cl_2NO$: C, 35.32; H, 5.33; Cl, 41.70; N, 8.24. Found: C, 35.02; H, 5.43; Cl, 42.01; N, 8.23. **N-tert-Butylacetamide (AcNH-*t*-Bu)**: mp 95–96 °C (lit.[17] mp 97–98 °C). **Acetanilide (AcNHPh)**: mp 115 °C (lit.[18] mp 115 °C). **N-Isopropylacrylamide (CH_2=CHCONH-*i*-Pr)**: mp 63–64 °C [lit.[19] mp 110–115 °C (2.0 kPa)]; IR (KBr) 1650 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.07 (d, 2 H, J = 6.4 Hz, $=CH_2$), 5.53 (t, 1 H, C*H*=), 5.20 (br, 1 H, N*H*), 3.26 (septet, 1 H, C*H*), 1.21 (d, 6 H, J = 6.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 172.3 (s, *C*=O), 134.1 (t, $=CH_2$), 128.6 (d, =*C*H), 43.4 (d, *C*H), 20.8 (q, CH_3); MS m/z 113 (M^+). Anal. Calcd for $C_6H_{11}NO$: C, 63.69; H, 9.80; N, 12.38. Found: C, 63.72; H, 9.82; N, 12.44. **N,N'-Dipropyladipoamide ($(CH_2CH_2CO)_2(NHPr)_2$)**: mp 164 °C (lit.[20] mp 164 °C). **N-tert-Butylbenzamide (BzNH-*t*-Bu)**: mp 133–134 °C; IR (KBr) 1630 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.7 (m, 5 H, aromatic *H*), 5.9 (br, 1 H, N*H*), 1.46 (s, 9 H, CH_3); ^{13} NMR ($CDCl_3$) δ 166.4 (s, *C*=O), 135.1 (s, ipso), 131.0 (d), 128.3 (d), 126.7 (d), 51.6 (s), 28.9 (q); MS m/z 177 (M^+). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found C, 74.49; H, 8.52; N, 7.90. **N-Phenyltrimethylacetamide (*t*-BuCONHPh)**: mp 130–131 °C (lit.[21] mp 132.5–133 °C). **Benzanilide (BzNHPh)**: mp 159–161 °C (lit.[22] mp 164–165 °C).

Amidation Method B. N-(2-Hydroxyethyl)acetamide ($AcNHCH_2CH_2OH$). To a mixture of Ph_3SbO (0.25 mmol), P_4S_{10} (0.75 mmol), and ethanolamine (20 mmol, 1.22 g) was added acetic acid (5 mmol) drop-by-drop with stirring and cooling. The mixture was then stirred at 50 °C for 1 h. After evaporation of excess ethanolamine in vacuo, workup similar to that described previously gave a slightly yellow viscous oil (yield 450 mg, 95%): bp 151 °C (0.7 kPa); IR (KRS-5) 1622 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (s, 1 H, N*H*), 3.85 (br, 1 H, O*H*), 3.69 (t, 2 H, J = 5.2 Hz, CH_2OH), 3.39 (t, 2 *H*, CH_2NH), 2.01 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 171.1 (s, *C*=O), 60.5 (t, *C*H_2OH), 41.8 (t, *C*H_2NH), 22.4 (q, CH_3); MS m/z 103 (M^+). Anal. Calcd for $C_4H_9NO_2$: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.60; H, 8.80; N, 13.57. **N-Propenylacetamide ($AcNHCH_2CH$=CH_2)**: bp 90 °C (0.7 kPa) [lit.[23] bp 130–131 °C (2.1 kPa)]. **N-tert-Butyltrimethylacetamide (*t*-BuCONH-*t*-Bu)**: bp 117–118 °C (0.7 kPa); IR (KBr) 1640 (amide (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.4 (br, 1 H, N*H*), 1.34 (s, 9 H, CH_3), 1.15 (s, 9 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 177.5 (s, *C*=O), 50.6 (s, $(CH_3)_3CN$), 38.9 (s, $(CH_3)_3CC$), 28.7 (q, $(CH_3)_3CN$), 27.7 (q, $(CH_3)_3CC$); MS m/z 157 (M^+). Anal. Calcd for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.68; H, 12.20; N, 8.89.

Dipeptide Synthesis (Method C). Z-Glycylglycine Ethyl Ester (Z-Gly-Gly-OEt). To a solution of Z-glycine (5 mmol, 1.05 g) in CH_2Cl_2 (10 mL) were slowly added, in order, Ph_3SbO (0.25 mmol, 92 mg), P_4S_{10} (1 mmol, 444 mg), and a solution of glycine ethyl ester hydrochloride (5 mmol, 698 mg) and Et_3N (5 mmol, 506 mg) in CH_2Cl_2 (10 mL). The mixture was stirred at 30 °C for 0.5 h. Workup was done with the general ethyl acetate extraction followed by washing with aqueous citric acid and neutralization. The dipeptide was then recrystallized from EtOAc/hexane: mp 81 °C (lit.[24] mp 80–81 °C). **Z-Phenylalanylleucine ethyl ester (Z-Phe-Leu-OEt)**: mp 102–103 °C (lit.[25] mp 110–111 °C); $[\alpha]^{20}_D$ -23.9° (*c* 1.0, EtOH) (lit.[25] $[\alpha]^{20}_D$ -24.7° (*c* 1.0, EtOH)). **Z-Leucylphenylalanine methyl ester (Z-Leu-Phe-OMe)**: mp 79–90 °C (lit.[26] mp 79–80 °C); $[\alpha]^{20}_D$ -19.2° (*c* 2.0, MeOH) $[\alpha]^{20}_D$ -19.3° (*c* 2.0, MeOH)). **Z-Serylglycine ethyl ester (Z-Ser-Gly-OEt)**: mp 105–107 °C; (lit.[25] mp 106–107 °C); $[\alpha]^{20}_D$ -5.8° (*c* 1.0, EtOH) (lit.[25] $[\alpha]^{20}_D$ -5.9° (*c* 1.0 EtOH)). **Z-Tyrocylglycine ethyl ester (Z-Tyr-Gly-OEt)**: mp 168–170 °C (lit.[27] mp 168–170 °C); $[\alpha]^{20}_D$ -23.5° (*c* 5.0, DMF) (lit.[27] $[\alpha]^{20}_D$ -23.6° (*c* 5.0, DMF)).

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Synthesis of Strained Aromatic Polycyclic Compounds via the Reaction of Arynes with Enolates of Cyclic Ketones

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The synthesis and characterization of polyphenylene derivatives continue to be topics of interest.[1] However, new partially hydrogenated polyphenylenes are only infrequently described in the literature. The latter compounds would be expected to interact with DNA or RNA.[2] Knowledge of such behavior would be useful for the design of new antitumor or antiviral agents.[3]

As a continuation of a program directed toward the synthesis of polycyclic benzocyclobutene derivatives and the study of their chemical and biological properties,[4] we sought to develop a new route to benzocyclobutabiphenylenes. Here, we report a new and convenient synthesis of such compounds. We also report some of their chemical properties.

Results and Discussion

A series of hexahydrobenzocyclobutabiphenylenes was obtained by the pathways shown in Scheme I.

When the complex base $NaNH_2$/*t*-BuONa[5] was replaced by $NaNH_2$, the attempted condensation of benzyne and the enolate **6** was unsuccessful. As previously reported,[6] this failure was probably due to the fact that **6** is not a good activating agent[7] for $NaNH_2$. It should also be noted that only the thermodynamically more stable of the two possible enolates of **7** was formed. It was reported[8] that complex bases favor such enolization.

The assigned structures of **5** and **8** were consistent with their IR, UV, ^1H NMR, and ^{13}C NMR spectra. The stereochemistry of **8** (Z = H) was deduced from the

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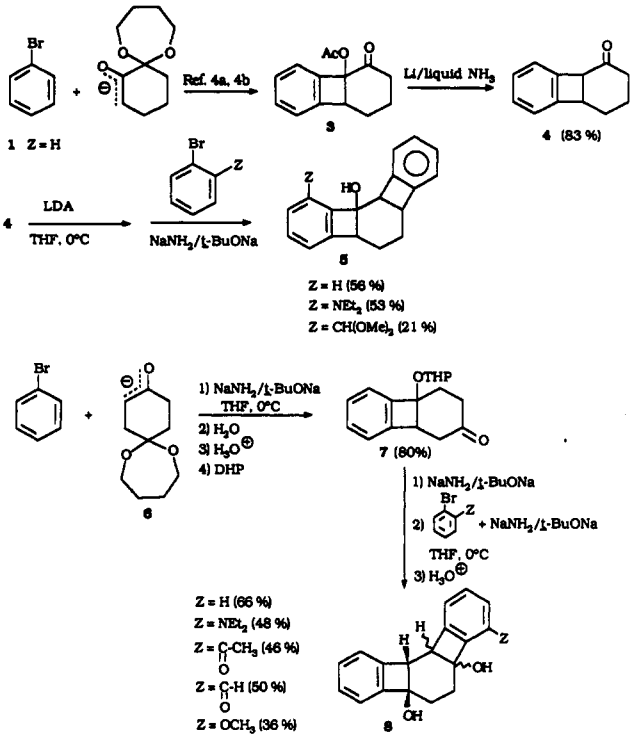
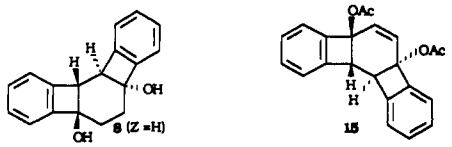
Scheme I



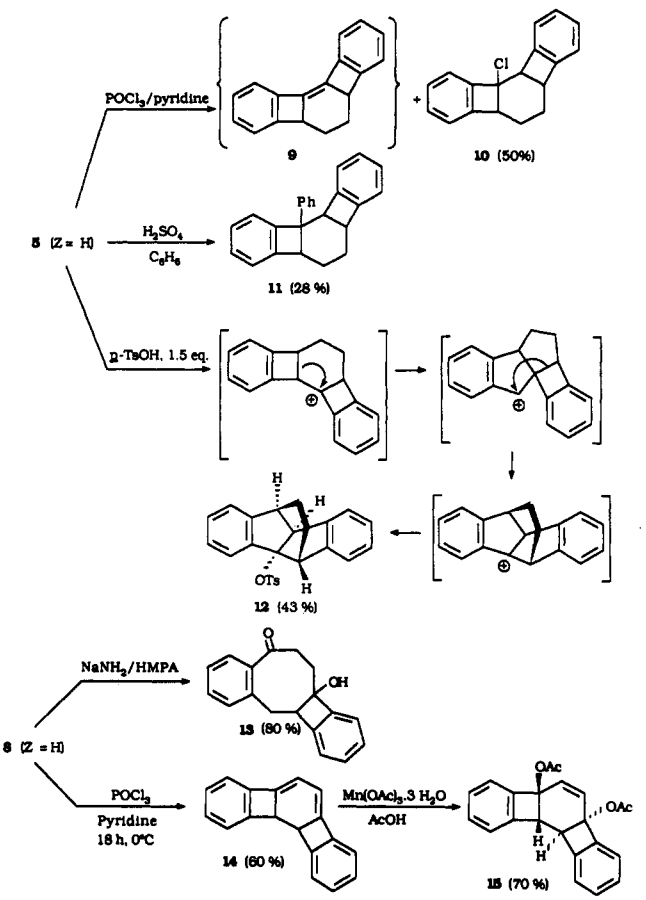
structure of the derivative **15**, the X-ray data of which has been collected.



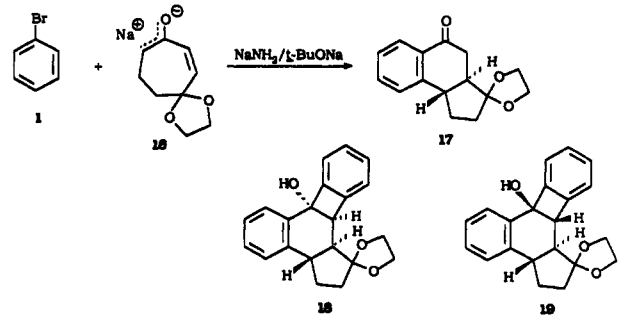
A few interesting chemical transformations of **5** (Z = H) and **8** (Z = H) are shown in Scheme II.

The formation of **10** and **11**, instead of **9**, indicated that the cation generated from **5** was relatively stable. (Notice that compound **9** was obtained only once with 24% yield, but unfortunately this compound was instable and so we just succeeded in performing its ^{1}H NMR spectra. Furthermore, all other attempts to synthetize this compound failed). In the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) (**5** (Z = H)) remained unchanged. However, an excess of the acid caused the transformation of **5** into **12**. Similar unusual nucleophilic behavior by *p*-TsOH was observed earlier.[9]

Scheme II



Scheme III



Scheme IV

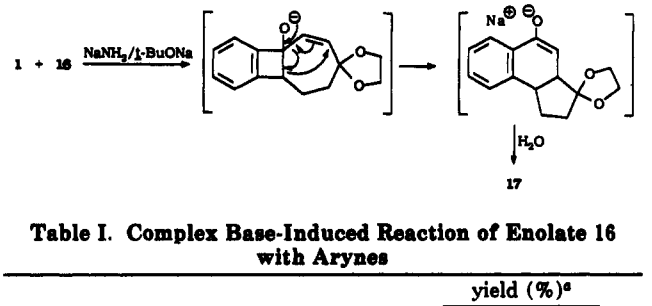


Table I. Complex Base-Induced Reaction of Enolate 16 with Arynes

solvent	*T* (°C)	*t* (h)	16/1	yield (%)[a] 17	18	19
DME	0	4	1:2	7	17	36
THF	25	4	1:2	9	14	30
DME	0	3	1:1	43	10	
THF	0	5	1:2	8	16	31

[a] Yield based on the parent ketone of **16**.

Compound **8** (Z = H) was easily transformed into **13** by treatment with strong base.[4c] However, the attempted

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base-catalyzed ring-opening of 13 was unsuccessful.

The dehydration of 8 (Z = H) to 14 was rather easily accomplished. However, the attempted dehydrogenation of 14 with DDQ,[10] Pd/C,[11] or $NiBr_2/Zn/DMF$[12] was unsuccessful. The relatively low aromatic character of the central ring of the expected dehydrogenation product[1c] could be partly responsible for this failure.

Interestingly the attempted dehydrogenation of 14 with $Mn(OAc)_3$[13] gave only the diacetate 15, the product of a 1,4-addition of an acetate free radical. A similar free radical reaction of $Mn(OAc)_3$ has been reported.[14]

The assigned structures of compounds 9 to 15 were consistent with their spectra. Also X-ray diffraction data were collected for compounds 12 and 15.

As expected, 14 was active in preventing ADN replication. Unexpectedly, so also was compound 15.[2] However, the nature of the interaction between these compounds and ADN remains to be determined.

A second series of polycyclic derivatives was also prepared (Scheme III).

Formation of 17 is shown in Scheme IV.

Similar rearrangements were observed[15] during the reaction of cyclohexenone enolates with arynes.

Compound 17 was obtained in 47% yield when stoichiometric amounts of 1 and 16 were used, whereas 18 (17%) and 19 (36%) were the main products when 2 equiv of 1 was used (Table I).

The structures of 17, 18, and 19 were established from their physical properties and by X-ray diffractometry.

Conclusion

The complex base-induced reaction of arynes with enolates of cyclic ketones proved useful for the synthesis of polycyclic aromatic compounds. The goal of applying this reaction to the synthesis of biologically active compounds is currently being pursued.

Experimental Section

General Methods. Melting points were determined on a Kofler melting point apparatus and are uncorrected. ^{13}C NMR spectra were recorded with a Brucker AM 400 or a Brucker 300 MHz spectrometer. ^1H NMR spectra were recorded on a JEOL PMX 60 at 60 MHz, a Bruker AW 80 at 80 MHz, or a Brucker AM 400 instrument at 400 MHz. Me_4Si was the internal standard. Infrared (IR) spectra of thin liquid films between NaCl plates or KBr pellets were recorded with a Perkin-Elmer 580 instrument. Elemental analyses were performed by CNRS Laboratory (Vernaison). Mass spectra were recorded by the Laboratory of Mass Spectroscopy, Faculté de Pharmacie (Nancy). Thin-layer chromatography (TLC) was performed with plates coated with kieselgel G (Merck). The plates were developed with petroleum ether/EtOAc. The silica gels used for column chromatography and flash chromatography were kieselgels of 0.063–0.2-mm and 0.04–0.063-mm particle size, respectively. High pressure liquid chromatography was performed with a Waters PREP 500 chromatograph equipped with a silica gel column. GLC analyses were performed with a Shimadzu GC-8A gas chromatograph equipped with a column packed with 10% SE-30 on Chromosorb WDMCS.

Materials. Sodamide powder (Merck) was mixed with the same weight of toluene and the mixture was kept under N_2. Before use, the mixture was centrifuged and the supernatant toluene was decanted. The sodamide was mixed with a small quantity of the reaction solvent. The mixture was centrifuged and the solvent was decanted. This sequence was repeated twice. Reagent-grade tetrahydrofuran (THF) (BASF) was distilled from sodium benzophenone ketyl. 1,2-Dimethoxyethane (DME) was distilled from sodium and was stored under sodium until used. The reaction of ketone enolates with arynes was performed as previously described.[4a,b] Compound 3 was prepared as previously described.[4a,c]

3,4,4a,8b-Tetrahydrobiphenylenone (4) was prepared as previously described.[16] Thus, to a mixture of 20 mL of liquid NH_3, 10 mL of THF, and 90 mg of Li was added drop by drop over 5 min a solution of 0.45 g of 3 and 10 mL of THF. The mixture was stirred until a blue color appeared; then the excess lithium was destroyed by the rapid addition of excess $PhCO_2Na$. The NH_3 was allowed to evaporate. The residue was washed with water and then was extracted with Et_2O. The extract was dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give 4: IR (NaCl) 1700 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.40–2.53 (m, 6 H, CH_2), 3.78–4.11 (m, 2 H, benzylic H), 6.80–7.25 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 18.45, 26.74 (CH_2); 40.55 (CH_2-C=O); 43.36 (CH); 53.50 (CHC=O); 121.93, 122.38, 128.10, 128.24, (Ar CH); 141.48, 147.06 (Ar C); 209.98 (C=O); UV (MeOH) λ (log ϵ) 268.1 (sh), 268.7 (3.20), 274 (3.15); mp (petroleum ether–ether) 54 °C. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.02. Found: C, 83.55; H, 7.17.

4b,5,6,6a,10b,10c-Hexahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylen-10b-ol (5) (Typical Procedure). The enolate of 4 was prepared by treatment of the ketone with LDA. Thus, a solution of diisopropylamine (22 mM) and THF (20 mL) under dry N_2 at 0 °C was treated with *n*-BuLi (1.6 M in hexane (14 mL)) (Aldrich). After 15 min, a solution of 4 (20 mM) and THF (10 mL) was added. To a solution of the complex base, prepared as previously described[4] ($NaNH_2$/*t*-BuONa = 80 mM/40 mM), was added the solution of the lithium enolate by syringe. Then bromobenzene (40 mM) was added at room temperature. Upon completion of the reaction, the mixture was poured onto ice and was extracted with Et_2O. The extract was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give 5: IR (KBr) 3600–3100 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.32–1.86 (m, 4 H, CH_2), 2.40–2.67 (m, 1 H, OH exchanged with D_2O), 3.23–3.67 (m, 2 H, $CHCH_2$), 4.00 (d (J = 5 Hz), 1 H, PhCHCHOH), 6.73–7.40 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.07, 21.70 (CH_2); 40.95, 47.07, 53.74 (C benzylic); 78.15 (C-OH); 120.57, 121.54, 123.01, 123.53, 127.19, 127.71, 127.74, 129.72 (Ar CH); 144.67, 145.26, 147.01, 148.64 (Ar C); UV (MeOH) λ (log ϵ) 264 (3.41), 268.5 (3.56), 274.1 (3.50); mp (petroleum ether–ether) 126 °C. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.96; H, 6.42.

2,3,3a,7b-Tetrahydro-3a-(tetrahydropyranyloxy)benzo[3,4]cyclobuta[1,2-*a*]biphenylenone (7) was prepared by treatment of the product of the reaction of ketone enolate 6 and benzyne[4a,b] with dihydropyran in CH_2Cl_2:[17] IR (KBr) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.30–2.55 (m, 10 H, aliphatic H), 2.65–2.90 (m, 2 H, aliphatic H), 3.20–4.20 (m, 3 H, O-CH_2, benzylic H), 4.85 (ps, 1 H, O-CH-O), 7.00–7.40 (m, 4 H, Ar H); UV (MeOH) λ (log ϵ) 261 (2,90), 266 (3,35), 273 (3,30); mp (petroleum ether): 78 °C.

4b,5,6,6a,10b,10c-Hexahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylene-4b,6a-diol (8, Z = H) was prepared by the reaction of the enolate of 7 and benzyne in the usual manner, followed by the removal of the tetrahydropyranyl protecting group by treatment with a catalytic amount of *p*-TsOH in methanol:[18] IR (KBr) 3500–3100 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.20–2.20 (m, 4 H, aliphatic H), 2.50–2.80 (m, 2 H, OH, exchangable with D_2O), 3.15 (s, 2 H, benzylic H), 7.10–7.50 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 30.48 (CH_2); 54.99 (CH_2); 79.70 (C-OH); 121.01, 122.42, 128.33, 129,85 (Ar CH); 144.01, 147.16 (Ar C); UV (MeOH) λ (log ϵ) 260.3 (3.12), 266.3 (3.30), 272.8 (3.30); mp (petroleum ether) 135 °C. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.43; H, 6.18.

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10b-Chloro-4b,5,6,6a,10b,10c-hexahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylene (10) and 4b,5,6,6a-Tetrahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylene (9). To a solution of 5 (2 mM) and pyridine (5 mL) was added $POCl_3$ (6 mM) at 0 °C. The mixture was maintained at ca. 0 °C for 2 h. Upon completion of the reaction (monitored by TLC), the mixture was poured onto ice and was extracted with Et_2O. The extract was washed with 10% aqueous HCl and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by centrifugal TLC on silica gel to give 10: ^1H NMR (CCl_4) δ 0.92–1.42 (m, 4 H, CH_2), 3.03–3.27 (m, 2 H, 2 x C*H*CH_2), 3.92 (d (J = 6 Hz), 1 H, C*H*CHCl), 6.85–7.47 (m, 8 H, Ar H); UV (MeOH) λ (log ε) 262.5 (3.38), 268.5 (3.41), 274.9 (3.38); mp (petroleum ether–ether) 161 °C. Anal. Calcd for $C_{18}H_{15}Cl$: C, 81.04; H, 5.66; Cl, 13.29. Found: C, 81.20; H, 5.65; Cl, 13.08; 9 was obtained once as explained in the text: ^1H NMR (CCl_4) δ 1.50–2.47 (m, 4 H, CH_2), 3.86–4.28 (m, 2 H, benzylic H), 6.67–7.52 (m, 8 H, Ar H).

4b,5,6,6a,10b,10c-Hexahydro-10b-phenylbenzo[3,4]cyclobuta[1,2-*a*]biphenylene (11). To a stirred solution of 5 (Z = H) (2 mM) and benzene (10 mL) were added 3 drops concentrated H_2SO_4. The mixture was refluxed for 3 h. Upon completion of the reaction (monitored by TLC), the mixture was cooled to room temperature, washed with water, and extracted with Et_2O. The extract was dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give 11: ^1H NMR (CCl_4) δ 1.06–1.37 (m, 4 H, CH_2), 3.10–3.48 (m, 2 H, C*H*CH_2), 3.97 (d (J = 6 Hz), 1 H, PhC*H*CPh), 6.65–6.90 (m, 1 H, Ar H), 6.90–7.25 (m, 12 H, Ar H); UV (MeOH) λ (log ε) 264.5 (3.24), 269.9 (3.30), 276.2 (3.25); mp (petroleum ether–ether) 180 °C. Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.53. Found: C, 92.95; H, 6.51.

1-(*p*-Tolulenesulfonyl)-3,4:7,8-dibenzotricyclo[3.3.2.0^{2,6}]decane (12) was prepared in the same manner as 11, but with p-TsOH (1.5 equiv) as the acid instead of H_2SO_4. 12: ^1H, NMR (CCl_4) δ 0.85–1.37 (m, 4 H, CH_2), 2.30 (s, 3 H, CH_3), 2.03–2.40 (m, 2 H, C*H*CH_2), 4.30 (d (J = 6 Hz), 1 H, PhC*H*CHPh), 6.57–7.80 (m, 12 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.40 (CH_3), 22.35, 26.27 (CH_2); 43.56, 49.39, 52.56 (C benzylic); 109.29 ($COS(O)_2$); 122.61, 122.84, 123.01, 126.59, 126.62, 127.28, 127.46, 129.07 (Ar CH); 135.49, 138.99, 139.92, 142.72, 143.44, 144.06 (Ar C); UV (MeOH) λ (log ε) 263 (sh); 271.2 (3.12); 277.4 (3.07); mp (EtOAc–ether) 198 °C. X-ray diffraction data were also collected.

8-Hydroxy-3,4:6,7-dibenzobicyclo[6.2.0]decanone (13) was prepared by a method previously described.[4a] 13: IR (KBr) 3500–3100 cm^{-1} (OH), 1650 (C=O); ^1H NMR ($CDCl_3$) δ 1.95–2.40 (m, 4 H, 2 × CH_2), 2.50–2.90 (m, 1 H, OH, exchangable with D_2O), 3.00–3.70 (m, 2 H, benzylic H), 7.10–7.80 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 35.64, 36.43, 41.90 (3 × CH_2); 59.98 (CH); 85.21 (COH); 123.74, 124.45, 127.87, 128.08, 128.81, 129.67, 131.29, 132.37 (Ar CH); 137.23, 139.82, 141.76, 144.98 (Ar C); 206.41 (C=O); UV (MeOH) λ (log ε) 248 (3.31), 271.5 (3.49), 286 (3.27); mp (petroleum ether–ether) 184 °C. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.49; H, 6.15.

10b,10c-Dihydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylene (14) was prepared by the same method as 10. 14: IR (KBr) 1620 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 3.85 (s, 2 H, benzylic H), 6.35 (s, 2 H, 2 × CH=C), 7.10–7.40 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$ δ 50.19 (CH); 113,71 (CH=); 119.56, 122.94, 128.14, 128.54 (Ar CH); 140.82, 144.36, 148.16 (Ar C, PhC=CH); UV (THF) λ (log ε) 214.2 (3.86), 247.2 (3.84), 298.8 (3.30); 355 (3.79); mp (petroleum ether–ether) 142 °C. Anal. Calcd for $C_{18}H_{12}$: C, 94.74; H, 5.26. Found: C, 94.43; H, 5.40.

4b,6a-Bis(acetyloxy)-4b,6a,10b,10c-tetrahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylene (15) was prepared by a method previously described.[19] 15: IR (KBr) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.90 (s, 6 H, 2 × CH_3), 4.20 (s, 2 H, benzylic H), 6.35 (s, 2 H, 2 × CH=C), 7.10–7.45 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.43 (CH_3); 50.75 (CH); 79.57 (C–O); 122.62, 123.68, 126.61, 128.28, 130.12 (CH=, Ar CH); 144.52, 146.30 (Ar C); 170.23 (C=O); mp (petroleum ether–ether) 220 °C. X-ray diffraction data were also collected.

Compound 16 was prepared in five steps from cycloheptanone. The first transformations (two steps) gave an α-ethylene ketal.[20] Allylic bromination of the ketal[21] and hydrolysis of the resulting bromide gave an allylic alcohol.[22] Compound 16 was obtained by oxidation of the alcohol.[23]

2,3-Benzobicyclo[4.3.0]nonanone-7-spiro-2′-[1,3]dioxolane (17) and 2,3:10,11-dibenzotricyclo[6.3.0.0^{1,9}]undecan-1-ol-7-spiro-2′-[1,3]dioxolane (18 and 19) were prepared by the reaction of the enolate 16 with benzyne. 17: IR (KBr) 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.65–1.85 (m, 1 H, CH), 2.00–2.50 (m, 3 H, CH_2, CH), 2.60–2.85 (m, 2 H, CH_2), 3.00–3.15 (m, 1 H, CH), 3.80–4.10 (m, 5 H, $O(CH_2)_2$, benzylic H), 7.20–7.60 (m, 3 H, Ar H), 8,00 (d, 1 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 25.90, 36.29, 38.91 (CH_2); 42.43, 50.31 (2 × CH); 64.97, 65.31 (OCO, OCH_2CH_2O); 116.02, 125.67, 126.72, 127.68, 132.18 (Ar CH); 133.65, 146.11, 198.49 (Ar C); mp (pentane) 112 °C. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 74.18; H, 6.77. X-ray diffraction data were also collected. 18: IR (KBr) 3500–3300 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.60–2.50 (m, 2 × CH_2, 2 × CH), 3.00 (s, 1 H, OH, exchangable with D_2O), 3.80–4.30 (m, $O(CH_2)_2$, CH), 6.90–7.50 (m, 7 H, Ar H), 7.95 (d, 1 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 26.46 (CH_2); 38.17 (CH_2); 39.38, 51.90, 55.20 (3 × CH); 64.42, 64.72 (OCH_2CH_2O); 79.36 (COH); 116.87 (OCO); 120.40, 124.86, 125.37, 126.59, 126.64, 126.98, 128.31, 129.21 (Ar CH); 139.91, 140.10, 142.31, 148.00 (Ar C); UV (MeOH) λ log (ε) 259.5 (2.96), 266.5 (3.09), 273.5 (3.06); mp (ether) 192 °C. Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.44; H, 6.34. X-ray diffraction data were also collected.

Supplementary Material Available: Experimental data for compounds 5, 8, and 19 and ORTEP diagrams of compounds 12, 15, 17, 18, and 19 (8 pages). Ordering information is given on any current masthead page.

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Solvent Effects on the Esterification of 2-Chloroethyl Compounds with Potassium Acetate

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Esters can be prepared by treating alkyl halides with metallic salts of carboxylic acids,[1-4] and the reaction proceeds smoothly in DMF[5] or DMSO.[5,6] The effects of dipolar aprotic solvents and hydrogen bonding on nucleophilic substitution reactions have been reported.[7,8] The reaction of benzyl chloride with sodium[9,10] or potassium acetate[11,12] is catalyzed by phase-transfer catalysts.

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